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*Interim Final Report*

## **PASSIVATION OF PIGMENT PARTICLES FOR THERMAL CONTROL COATINGS**

*By:* K. M. SANCIER S. R. MORRISON E. P. FARLEY

*Prepared for:*

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
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SRI Project PYU-7083

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## INTRODUCTION

Zinc orthotitanate has been identified as a promising candidate pigment for thermal control coatings. The pigment exhibited good photostability in simulated space environmental tests.<sup>1</sup> The plasma calcining treatment increased the photostability of the pigment.<sup>2</sup> In addition, the application of redox couple additives to the surface of the pigment increased its photostability.<sup>3</sup> The work encompassed by these studies was performed on a zinc orthotitanate pigment made by calcining the separate oxides.

A new process for manufacturing larger quantities of the zinc orthotitanate pigment has been devised by the IIT Research Institute (IITRI). This process consists of calcining a coprecipitated mixture of zinc oxalate and titanium oxalate.<sup>4</sup>

The current program was designed to examine the increased photostability of the coprecipitated pigment that is provided by:

- . the application of redox couple surface additives that were successful with an earlier pigment (thermal decomposition of the mixed oxides).
- . Plasma calcining.

## SCOPE OF WORK

The objectives of the research effort are to:

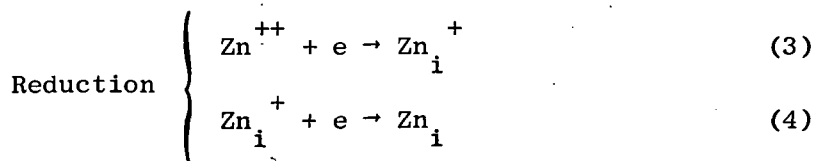
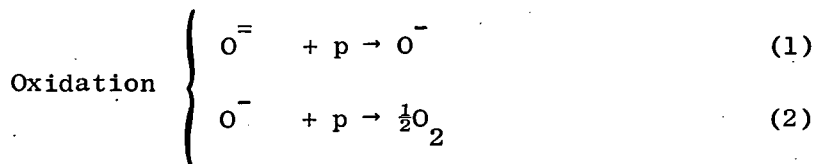
- (1) Study the passivation of coprecipitated zinc orthotitanate accomplished by applying surface additives to achieve the ultimate goal of providing a pigment that will be stable under ultraviolet radiation in vacuum
- (2) Investigate various surface additives to identify the one most effective in stabilization
- (3) Investigate the effects of concentration of additive and methods of application to the pigment surface to optimize the surface coating.

## BACKGROUND

The surface additive approach, developed for NASA, has been applied to increase the stability of zinc orthotitanate and of ZnO against damage under vacuum-ultraviolet conditions and to passivate the ZnO pigment against photointeractions with the polymer binder.<sup>3,5,6</sup> The approach has also been used in preliminary work sponsored by SRI to provide increased photostability of polymer films containing ZnO or TiO<sub>2</sub>.

### Mechanism of Radiation Damage

The mechanism of the protective action of surface additives has been discussed in detail.<sup>3,5-8</sup> We will briefly review the probable mechanism of radiation damage. In the case of ultraviolet radiation, photodamage to pigments is initiated by electronic charge carriers--electrons and holes--that are produced when the semiconductor pigment absorbs photons of energy equal to or greater than the bandgap. The chemical damage ensues from interactions of the electrons and holes with the lattice ions. For example, in the case of the ZnO phase, the following reactions are believed to occur:



In reactions (1) and (2), the photoproduced holes  $p$  oxidize lattice oxygen ions  $\text{O}^{\cdot -}$  to oxygen that may leave the solid. In reactions (3) and (4), the photoproduced electrons  $e$  reduce the zinc lattice ions  $\text{Zn}^{++}$

and result in excess zinc which becomes interstitial zinc,  $Zn_i^+$  or  $Zn_i$ . The coloration of the pigment is believed to be caused by the excess interstitial zinc that has limited solubility in the lattice. This excess zinc either causes mechanical strain in the lattice or it precipitates at defects such as dislocations.

In zinc orthotitanate, the lattice titanium ions  $Ti^{+4}$  are expected to be reduced by photoproduced electrons according to



and to give rise to the  $Ti^{+3}$  color centers (or to the electrical equivalent, oxygen ion vacancies). It is of significance that the photoproduced species  $Zn_i^+$  and  $Ti^{+3}$  are paramagnetic. Thus, we have used electron spin resonance to detect the presence of these species in zinc orthotitanate.

#### Mechanism of Surface Additive Protection

Inorganic surface additives increase the photostability of pigments by serving as recombination centers for the photoproduced charge carriers that otherwise would produce chemical damage. The mechanism of the process of recombining electrons and holes can be illustrated by the ferro/ferricyanide ( $Fe^{++}/Fe^{+++}$ ) redox couple that was found effective in protecting ZnO.



No net change occurs in the amount of the two forms of the additive, and the photoproduced electrons and holes have been recombined; hence, they do not react chemically with lattice ions.

To be an effective recombination center, we established in an earlier program<sup>5</sup> that:

- . The surface additive must be a one-equivalent redox couple and be present in both valence states.
- . The oxidized valence state must have a high capture cross section for electrons.
- . The reduced valence state must have a high capture cross section for holes.
- . The surface state energy level of the additive must be in the forbidden gap of the semiconductor pigments.
- . The additive must be chemically and photochemically stable and nonvolatile.

Very low concentrations of a redox surface additive can provide protection against vacuum photodamage. In the case of zinc orthotitanate prepared by thermal decomposition of the individual oxides,  $10^{-3}$  monolayers of iron cyanide or iridium hexachloride additives produced significant passivation compared with the blank.<sup>3</sup> A cerium redox additive, which was in an acid solution to maintain solubility of the cerium salt, provided passivation even at  $10^{-6}$  monolayer coverage. The specific action of the cerium additive could not be directly evaluated because the acid solution itself passivated the pigment, presumably because the acid leached excess ZnO from the zinc orthotitanate pigment.

The high recombination efficiency at such low surface coverages of additives can be accounted for on the basis that the charge carriers have long diffusion paths, about one micrometer in ZnO. Since this distance is the order of magnitude of the diameter of most pigment particles, it is evident that large volumes of the crystal can be swept free of charged carriers.

### Degradation Measurement Techniques

The ESR technique has been used in both current and earlier studies for investigating the influence of surface additives on photodamage to pigments such as zinc orthotitanate. This technique permits study of the characteristic photodamage centers ( $\text{Zn}_i^+$  and  $\text{Ti}^{+3}$ ) in the pigment as powders as well as pigmented coatings. In the case of zinc orthotitanate samples that we have examined, the ESR spectra contain two principal lines: one at a g value of 1.94 associated with the donors ( $\text{Zn}_i^+$  and/or conduction electrons) usually found in  $\text{ZnO}$ , and the other at a g value of 1.974 probably associated with the  $\text{Ti}^{+3}$  species.



## EXPERIMENTAL DETAILS

### Pigment Preparation

The zinc orthotitanate pigment used in these studies is IITRI's sample designated LH-101 (6-12). This was prepared by calcination at 1200°C for two hours.

To apply the surface additives to the pigment, a slurry was made of the pigment (2 g) with a solution (4 ml) containing a known concentration of the appropriate inorganic salts. The slurry was centrifuged, the supernatant liquid poured off, and the solid was dried at 140°C for 15 hours in vacuum. Three additive redox couples were studied:  $\text{Fe}(\text{CN})_6^{-4}/\text{Fe}(\text{CN})_6^{-3}$ ,  $\text{IrCl}_6^{-3}/\text{IrCl}_6^{-2}$ , and  $\text{Ce}^{+3}/\text{Ce}^{+4}$ . The solution added to a pigment aliquot contained equal molar concentration ( $10^{-3}$  or  $10^{-2}$  M) of the salts of two valence states of a given redox couple. The salts used were  $\text{K}_4\text{Fe}(\text{CN})_6$ ,  $\text{K}_3\text{Fe}(\text{CN})_6$ ,  $\text{K}_3\text{IrCl}_6 \cdot 3\text{H}_2\text{O}$ ,  $\text{K}_2\text{IrCl}_6$ ,  $\text{Ce}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ , and all were of reagent grade. The solutions of the iron cyanide [ $\text{Fe}(\text{CN})_6^{-4}/\text{Fe}(\text{CN})_6^{-3}$ ] and iridium chloride [ $\text{IrCl}_6^{-3}/\text{IrCl}_6^{-2}$ ] additives were at pH 6 or 7, while that of the cerium additive contained 1N perchloric acid to maintain the cerium ions soluble.

The surface coverage of additive on the pigment was calculated from the solution concentration, the hold-up of the solution after centrifuging (0.35 ml/g pigment), the surface area of the pigment (assuming about  $10^2 \text{ m}^2/\text{g}$ ), and with the assumption of a surface site density of  $10^{15}$  sites/ $\text{cm}^2$ . Calculation of the surface coverage  $\theta$  in monolayers of the additive in each valence state shows it to be equal numerically to twice the molarity of the additive in each valence state in the solution used to treat the pigment. This calculation assumes no preferential removal by the pigment of either valence state.

## Vacuum Photolysis

The additive-treated pigments were maintained at low pressure ( $10^{-7}$  to  $10^{-8}$  torr) during ultraviolet irradiation. The pigments were introduced into a quartz tube (3 mm i.d.) in a column about 4 cm high. This tube was fused to a 2  $\ell$ /sec Vac-Ion pump (Varian), and to a roughing pump (oil diffusion with two traps in liquid nitrogen). The pigment was heated to 125°C for 1.5 hours while pumping to about  $10^{-5}$  torr. Then the Vac-Ion pump was started and the sample Vac-Ion assembly was sealed off from the roughing pump, and the sample was cooled.

Ultraviolet irradiation was carried out with a concentrated mercury arc (PEK Type 212 with quartz optics of f/0.5) at a distance of 24 inches. Irradiation was at room temperature for three hours, and the sample became only slightly warm to touch ( $<40^{\circ}\text{C}$ ).

## ESR Equipment

The ESR spectra were measured with an X-band spectrometer (Varian V-4502) equipped with a dual cavity, 12-inch magnet Fieldial, and a dual cavity ( $\text{TE}_{104}$ ) operated from the microwave bridge in the lower power mode. The tube containing the pigment was situated in the cavity with a screen window through which the ultraviolet light was focused. This cavity was modulated at  $10^5$  Hz with an amplitude of 10 Oe. The other cavity contained a sample of 0.1% carbon in KCl (Varian) for monitoring cavity sensitivity and measuring g-value. This cavity was modulated at 400 Hz.

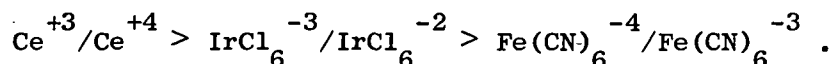
For the vacuum photolysis study, ESR measurements were made at 77°K by use of a quartz dewar with liquid nitrogen into which the sample was placed. Because of slow temperature equilibration of the pigment at the low ambient pressure in the tube, the sample in liquid nitrogen had to be precooled for one hour before ESR measurements.

## RESULTS AND DISCUSSION

The photodamage effects of the pigment LH-101 (6-12) with and without various surface redox additives could be evaluated only from the ESR line at a  $g$  value of 1.94. The other ESR line of interest, at a  $g$  value of 1.97, could not be studied because it was overlapped by an intense resonance caused by a paramagnetic impurity with a  $g$  value at 2.08. Based on its line shape and  $g$  value, this impurity is probably from  $\text{Cu}^{++}$ ; this is confirmed as such in conversations with Mr. Y. Harada of IITRI who had reason to suspect copper contamination in this pigment batch. This impurity was not detected in another IITRI batch, LH-102 (6-12) sent to SRI. At the request of the Project Monitor additive effects on this latter batch were not studied until the cause of the impurity was identified.

The photodamage to the pigment and the effects of the various surface additives are summarized in Table 1. The intensity of the ESR line ( $g = 1.94$ ) before irradiation is  $I_0$ ,  $I$  is the intensity after 3 hours in vacuum, and  $\Delta I$  is the increase in intensity of this ESR line because of photodamage.

The order of effectiveness of the redox additives in protecting the pigment for photolysis is most clearly seen by comparing the results for the additive at the lower concentration,  $10^{-3}$  milliequivalents of each valence state per gram of pigment. Such a surface concentration is equivalent to about 0.06 monolayers of each valence state. At this concentration, the order of decreasing effectiveness of the additives is then



At the higher concentration, both the cerium and the iridium chloride additives prevented any photodamage.

It is evident that a blank run with the pigment exposed to 1N HClO<sub>4</sub> did not provide protection to the pigment. This result is in contrast to that reported in our earlier study.<sup>3</sup> We may therefore tentatively conclude that in the coprecipitated pigment, there is very little excess ZnO phase to be extracted by acid, and thus very little available to be photolyzed. The somewhat greater photolysis rate of the more dilute iron cyanide additive ( $\Delta I = 11$ ) than that of the water-blank ( $\Delta I = 7$ ) may represent the limits of precision of the results.

## CONCLUSIONS AND RECOMMENDATIONS

The ESR analyses have shown that certain surface additives passivate the zinc orthotitanate pigment produced by calcining the coprecipitate of the oxalates of zinc and titanium. The evaluation of passivation, however, was restricted to photoproduction of the damage center at a g value of 1.94 (ZnO-type defects). An unintentional paramagnetic impurity, probably  $\text{Cu}^{+2}$ , in the pigment sample that was provided to us prevented evaluation of the passivation of the damage center at a g value of 1.97 ( $\text{Ti}^{+3}$ -type defects).

Within these restrictions, the cerium surface redox additive completely passivated the pigment at both surface concentrations examined--0.06 and 0.6 monolayers of each valence state. Somewhat less passivation was provided by the iridium chloride redox couple and even less by the iron cyanide redox couple.

In future work, the efficiencies of these additives should be evaluated for their passivation of photodamage centers of both types. Toward NASA's goals of obtaining a superior passivated pigment, the additive approach should also be evaluated on the coprecipitated pigment that is plasma calcined.

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Table 1

## PHOTODAMAGE TO ZINC ORTHOTITANATE PIGMENT LH-101 (6-12)

Additive		ESR Peak Intensity 1.94-Resonance*		
Couple	Concentration <sup>†</sup>	I <sub>o</sub>	I	ΔI
Blank - H <sub>2</sub> O	0	10	17	7
Blank - 1 N HClO <sub>4</sub>	0	12	16	4
Ce <sup>+3</sup> /Ce <sup>+4</sup> , 1 N HClO <sub>4</sub>	10 <sup>-3</sup>	0	0	0
Ce <sup>+3</sup> /Ce <sup>+4</sup> , 1 N HClO <sub>4</sub>	10 <sup>-2</sup>	0	0	0
IrCl <sub>6</sub> <sup>-3</sup> /IrCl <sub>6</sub> <sup>-2</sup>	10 <sup>-3</sup>	0	3	3
IrCl <sub>6</sub> <sup>-3</sup> /IrCl <sub>6</sub> <sup>-2</sup>	10 <sup>-2</sup>	2	2	0
Fe(CN) <sub>6</sub> <sup>-4</sup> /Fe(CN) <sub>6</sub> <sup>-3</sup>	10 <sup>-3</sup>	4	15	11
Fe(CN) <sub>6</sub> <sup>-4</sup> /Fe(CN) <sub>6</sub> <sup>-3</sup>	10 <sup>-2</sup>	3	5	2

\* Measured at 77 K in arbitrary units; irradiation in vacuum at room temperature for 3 hours. I<sub>o</sub> - before irradiation, I - after 3 hours irradiation, ΔI increase caused by irradiation.

<sup>†</sup> Concentration of each valence state of additive in milliequivalents/g pigment.